



## Early Journal Content on JSTOR, Free to Anyone in the World

This article is one of nearly 500,000 scholarly works digitized and made freely available to everyone in the world by JSTOR.

Known as the Early Journal Content, this set of works include research articles, news, letters, and other writings published in more than 200 of the oldest leading academic journals. The works date from the mid-seventeenth to the early twentieth centuries.

We encourage people to read and share the Early Journal Content openly and to tell others that this resource exists. People may post this content online or redistribute in any way for non-commercial purposes.

Read more about Early Journal Content at <http://about.jstor.org/participate-jstor/individuals/early-journal-content>.

JSTOR is a digital library of academic journals, books, and primary source objects. JSTOR helps people discover, use, and build upon a wide range of content through a powerful research and teaching platform, and preserves this content for future generations. JSTOR is part of ITHAKA, a not-for-profit organization that also includes Ithaka S+R and Portico. For more information about JSTOR, please contact [support@jstor.org](mailto:support@jstor.org).

## THE GASES IN ROCKS<sup>1</sup>

---

R. T. CHAMBERLIN  
The University of Chicago

---

It has been known for a long time from microscopic studies that some minerals inclose minute cavities which contain both liquid and gaseous matter. For a much shorter period it has been known that various igneous rocks, when exposed to red heat in a vacuum, evolve several times their volume of gas, and that this gas is of quite variable composition. Since these gases occur in proportions entirely different from those of the constituents of the air, it has not seemed probable that they were derived directly from our present atmosphere, unless the rocks manifest some power of selective absorption not now understood. The apparent difficulties involved in this conception have suggested that some earlier atmosphere was rich in those gases. This involves a hypothesis relative to the changes through which the atmosphere has passed, and leads on to a theory of its origin and that of the earth itself. An alternative hypothesis regards these gases, not as the products absorbed by a molten earth from its surrounding gaseous envelope, but as entrapped in the body of the earth during its supposed accretion, and hence as a source from which accessions to our present atmosphere might be derived. A study of the gases in the rocks has seemed, therefore, to give promise of results of some value to atmospheric problems and, perhaps, to those of cosmogony. Because of this, it has appeared advisable to determine more widely the range and the distribution of these gases, their relations to other geologic phenomena, and the states in which the gases, or gas-producing substances, exist in the rocks.

### THE ANALYSES CLASSIFIED

In these studies the gases were extracted for analysis by heating the powdered rock material to redness in a vacuum and pumping off

<sup>1</sup> This paper presents in a brief form some of the results discussed at greater length in "The Gases in Rocks," *Publication No. 106* of the Carnegie Institution of Washington. For a detailed description of the analyses, a discussion of the chemical aspects of the problem, and an outline of the work previously done in this field, recourse must be had to the original paper.

the evolved gas. In all, 112 complete analyses were made besides numerous special or partial analyses connected with various experiments. These may perhaps be most advantageously and briefly shown when collected into groups. To make these tables as complete as possible, not only the results of the author's studies, but all the available analyses of other investigators, have been included in the lists. Except in the case of four of the five analyses by Tilden, relative to which sufficient data are not given, all of the figures in these tables refer to volumes of gas per volume of rock. Previous investigators have usually given the total volume of gas and the percentages of each constituent. From these I have calculated the volumes for each individual gas. The numbers in the first column are the analysis numbers used in Table 8 of the original paper.<sup>1</sup>

In making the averages of the analyses, it should, perhaps, be stated that in those cases where, on account of excessive carbonation of the rocks, no figures are given for carbon dioxide, the average amount of this gas calculated from the other analyses is assumed to be present. This addition is made to the average total and makes this figure slightly greater than the average of the column which it foots. The same method has been used for carbon monoxide in the three of Travers' analyses where carbon monoxide and hydrogen are put together.

The figures for the Orgueil meteorite which yielded such a remarkable amount of sulphur dioxide make the average for the sulphur gases an abnormal one. The presence of this gas in quantity must mean that the meteorite has suffered much from weathering and oxidation subsequent to its fall. Considerable troilite has passed into iron sulphate which has been decomposed by the heat of the combustion-furnace.

Omitting the sulphur dioxide of this specimen, the average total volume of gas from stony meteorites is reduced to 4.80 times the volume of the meteoritic material.

Methane was determined in only two of these analyses. In these two it averaged 0.10 volume; but in order to make the figures consistent in the table, it was necessary to average these as if the eight other meteorites yielded no marsh-gas, though it is highly probable

<sup>1</sup> *Carnegie Publication No. 106*, pp. 14-22.

TABLE I  
ANALYSES CLASSIFIED BY GROUPS OF ROCKS

| No. | Rock and Locality                              | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|-----|------------------------------------------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|------------|
|     | <i>Granites and gneisses of igneous origin</i> |                  |                 |      |                 |                |                |       |            |
|     | Granite, Skye (per cent.).....                 | .....            | 28.60           | 6.45 | 3.02            | 61.68          | 5.13           | 99.88 | Tilden     |
|     | Granite, Vire (average).....                   | 0.05             | .86             | .35  | .12             | 5.29           | .04            | 6.71  | Gautier    |
| 1   | Granitoid porphyry, L'Esterel.....             | .....            | 4.50            | .32  | .19             | 2.36           | .10            | 7.53  | Do         |
| 2   | Medium-grained, white granite.....             | .....            | .28             | .07  | .07             | .92            | .10            | 1.44  | Chamberlin |
| 3   | Coarse-grained, reddish granite.....           | .....            | .42             | .09  | .10             | 2.94           | .11            | 3.66  | Do         |
| 4   | Laurentian gneiss, Ontario.....                | .....            | .31             | .08  | .06             | 1.50           | .13            | 2.08  | Do         |
| 9   | Pike's Peak granite.....                       | .....            | .37             | .05  | .02             | .04            | .12            | .60   | Do         |
| 19  | Granite porphyry, Menominee.....               | .....            | 3.51            | .72  | .06             | 2.34           | .22            | 6.85  | Do         |
| 20  | Fine-grained gneiss, Menominee.....            | tr.              | 1.89            | .23  | .02             | .43            | .23            | 2.80  | Do         |
| 21  | Fine-grained banded gneiss, Menominee.....     | .....            | 6.63            | 1.13 | .06             | 1.37           | .08            | 9.27  | Do         |
| 22  | Laurentian granite, Marquette.....             | .....            | 1.89            | .13  | .03             | .74            | .15            | 2.94  | Do         |
| 24  | Pink granite, North Carolina.....              | tr.              | .16             | .05  | .02             | .38            | .04            | .65   | Do         |
| 25  | Gray granite, Quincy, Mass.....                | tr.              | .39             | .09  | .06             | 1.04           | .02            | 1.60  | Do         |
| 26  | Gray granite, Russia.....                      | tr.              | 1.79            | .18  | .....           | .99            | .....          | 2.96  | Do         |
| 33  | Laurentian gneiss, Marquette.....              | tr.              | .85             | .15  | .07             | 1.79           | .12            | 2.98  | Do         |
| 37  | Oglesby blue granite, Georgia.....             | tr.              | 1.13            | .11  | .03             | 1.06           | .05            | 2.38  | Do         |
| 38  | Stone Mountain granite, Georgia.....           | tr.              | .08             | .03  | .01             | .60            | .04            | .76   | Do         |
| 39  | Ortonville granite, Minn.....                  | tr.              | 1.20            | .05  | .01             | .05            | .05            | 1.36  | Do         |
| 57  | Granite porphyry bowllder, New York.....       | .04              | carb.           | .27  | .02             | .85            | .04            | 1.22  | Do         |
| 66  | Gneiss of igneous origin, Ontario.....         | tr.              | .28             | .13  | .03             | .95            | .08            | 1.47  | Do         |
|     | Average of 19 analyses.....                    | tr.              | 1.47            | .22  | .05             | 1.36           | .09            | 3.19  |            |
|     | <i>The syenite group</i>                       |                  |                 |      |                 |                |                |       |            |
| 44  | Nephelite syenite, Ontario.....                | .....            | 0.29            | 0.05 | 0.04            | 0.25           | 0.05           | 0.68  | Chamberlin |
| 51  | Shonkinite, Highwood Mountains, Mont.....      | tr.              | .11             | .06  | .05             | .95            | .05            | 1.22  | Do         |
| 53  | Quartz syenite porphyry, Colorado.....         | .....            | carb.           | .11  | .08             | .22            | .03            | .44   | Do         |
| 56  | Hornblende syenite, Maine.....                 | tr.              | .15             | .07  | .03             | 2.22           | .03            | 2.50  | Do         |
|     | Average of 4 analyses.....                     | tr.              | .18             | .07  | .05             | .91            | .04            | 1.25  |            |

TABLE I—Continued

| No. | Rock and Locality                     | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total  | Analyst    |
|-----|---------------------------------------|------------------|-----------------|------|-----------------|----------------|----------------|--------|------------|
|     | <i>The gabbro-diorite group</i>       |                  |                 |      |                 |                |                |        |            |
|     | Gabbro, Lizard, England (per cent.)   | .....            | 5.50            | 2.16 | 2.03            | 88.42          | 1.90           | 100.01 | Tilden     |
| 15  | Gabbro, Isle of Skye                  | .....            | .00             | .00  | .....           | 1.40           | .....          | 1.40   | Travers    |
| 16  | Gabbro, summit of Mt. Sneffels, Colo. | .....            | .40             | .10  | .04             | 1.13           | .14            | 1.81   | Chamberlin |
| 17  | Gabbro, summit of Mt. Sneffels        | .....            | carb.           | .12  | .02             | .97            | .12            | 1.23   | Do         |
| 32  | Orthoclase gabbro, Duluth             | .....            | .44             | .12  | .07             | 2.68           | .33            | 3.04   | Do         |
| 36  | Schistose gabbro, Menominee           | 0.02             | 20.07           | .58  | .20             | 8.54           | .32            | 29.73  | Do         |
| 52  | Olivine gabbro, Duluth                | tr.              | .16             | .07  | .04             | .52            | .05            | .84    | Do         |
| 58  | Theralite, Crazy Mountains, Mont.     | tr.              | 1.08            | .17  | .04             | .93            | .03            | 2.25   | Do         |
| 60  | Intrusive, Highwood Mountains, Mont.  | .....            | .28             | .07  | .04             | .45            | .03            | .87    | Do         |
| 73  | Diorite plug in shales, Colorado      | .03              | .22             | .06  | .05             | 1.10           | .06            | 1.52   | Do         |
| 74  | Coarse diorite boulder, Maine         | .06              | .27             | .07  | .04             | 1.29           | .05            | 1.78   | Do         |
|     | Diorite, Penobscot Bay, Me.           | .07              | .21             | .04  | .20             | 3.95           | .14            | 4.61   | Do         |
|     | Average of 11 analyses                | .02              | 2.31            | .13  | .07             | 2.09           | .11            | 4.73   |            |
|     | <i>Diabases and basalts</i>           |                  |                 |      |                 |                |                |        |            |
|     | Basalt, Antrim                        | .....            | 2.57            | 1.61 | 0.80            | 2.80           | 0.13           | 8.00   | Tilden     |
|     | Ophite, Villefranche (average)        | .24              | 2.39            | .33  | .08             | 4.52           | .02            | 7.58   | Gautier    |
| 11  | Lherzolite, Lherz                     | 1.86             | 12.29           | .31  | tr.             | 1.15           | tr.            | 15.61  | Do         |
| 34  | Keweenaw diabase, Wisconsin           | .....            | .59             | .05  | .19             | 3.83           | .25            | 4.91   | Chamberlin |
| 35  | Keewatin greenstone, Mesabi           | .19              | 20.08           | 1.16 | .09             | 10.10          | .57            | 32.19  | Do         |
| 45  | Keweenaw diabase, Minnesota           | .01              | .25             | .06  | .06             | 3.15           | .06            | 3.59   | Do         |
| 50  | Iron basalt, Greenland                | tr.              | 3.74            | 1.74 | .17             | 2.24           | .16            | 8.05   | Do         |
| 61  | Nephelite melilitite basalt, Texas    | .05              | 1.07            | .20  | .06             | 1.16           | .10            | 2.64   | Do         |
| 84  | Diabase, Nahant, Mass.                | .19              | 4.91            | .21  | .12             | 3.13           | .15            | 8.71   | Do         |
| 85  | Vogesite, La Plata, Colo.             | .....            | carb.           | .14  | .03             | 1.08           | .05            | 1.30   | Do         |
| 110 | Keweenaw diabase, Michigan            | tr.              | 1.31            | .09  | .09             | 2.34           | .05            | 3.88   | Do         |
| 111 | Basalt of 1868, Kilauea, Hawaii       | .01              | .60             | .18  | .02             | .02            | .02            | .85    | Do         |
| 112 | Lava of 1906, Vesuvius                | .03              | .31             | .05  | .01             | .01            | .01            | .42    | Do         |
|     | Lava of 1906, Vesuvius                | .14              | .39             | .05  | .02             | .01            | .01            | .62    | Do         |
|     | Average of 14 analyses                | .19              | 3.96            | .44  | .12             | 2.54           | .11            | 7.36   |            |

TABLE I—Continued

| No.                             | Rock and Locality                    | H <sub>2</sub> S | CO <sub>2</sub> | CO    | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|---------------------------------|--------------------------------------|------------------|-----------------|-------|-----------------|----------------|----------------|-------|------------|
| <i>Andesites</i>                |                                      |                  |                 |       |                 |                |                |       |            |
| 13                              | Andesite, Ouray Co., Colo.           | .....            | carb.           | 0.09  | 0.02            | 0.08           | 0.08           | 0.27  | Chamberlin |
| 47                              | Andesite, Red Mountain, Ariz.        | tr.              | 5.12            | .57   | .30             | .12            | .26            | 6.37  | Do         |
| 62                              | Andesite, Rosita Hills, Colo.        | tr.              | carb.           | .27   | .05             | .30            | .13            | .75   | Do         |
| 64                              | Andesite, Lipari Islands.            | tr.              | .56             | .04   | .01             | .17            | .02            | .80   | Do         |
| 70                              | Andesite, Granite Mountain, Utah.    | tr.              | 2.66            | .16   | .03             | .53            | .05            | 3.43  | Do         |
| 72                              | Phonolite trachyte, Pike's Peak.     | tr.              | .76             | .05   | .03             | .19            | .06            | 1.08  | Do         |
| 91                              | Andesite, summit of Orizaba.         | .....            | .22             | .05   | .00             | .01            | .03            | .31   | Do         |
|                                 | Average of 7 analyses.               | .....            | 1.86            | .18   | .06             | .20            | .09            | 2.39  |            |
| <i>Rhyolites</i>                |                                      |                  |                 |       |                 |                |                |       |            |
| 10                              | Rhyolite, Marble Mountain, Arizona.  | .....            | 0.22            | 0.08  | 0.04            | 0.03           | 0.13           | 0.50  | Chamberlin |
| 49                              | Rhyolite vitrophyre, Telluride.      | .....            | 2.33            | .05   | .03             | .07            | .03            | 2.51  | Do         |
|                                 | Pitchstone rhyolite, Rosita Hills.   | .....            | .07             | ..... | .13             | .....          | .....          | .20   | Do         |
| 59                              | Nevadite, Chalk Mountain, Colo.      | .....            | .15             | .06   | .01             | .02            | .03            | .27   | Do         |
|                                 | Average of 4 analyses.               | .....            | .69             | .05   | .02             | .06            | .05            | .87   |            |
| <i>Schists</i>                  |                                      |                  |                 |       |                 |                |                |       |            |
| 3                               | Keewatin schist, Mesabi.             | .....            | 7.67            | 0.28  | 0.05            | 3.81           | 0.22           | 12.03 | Chamberlin |
| 23                              | Schist with chloritoid, Black Hills. | .....            | .46             | .10   | .04             | 3.97           | .05            | 3.72  | Do         |
|                                 | Average.                             | .....            | 4.06            | .19   | .05             | 3.44           | .13            | 7.87  |            |
| <i>Miscellaneous porphyries</i> |                                      |                  |                 |       |                 |                |                |       |            |
| 14                              | Coarse porphyry, Ouray Co., Colo.    | .....            | carb.           | 0.05  | 0.02            | 0.22           | 0.01           | 0.30  | Chamberlin |
| 78                              | Topaz quartz-porphyry, Saxony.       | .....            | .32             | .08   | .05             | .44            | .08            | .97   | Do         |
|                                 | Average.                             | .....            | .32             | .06   | .04             | .33            | .04            | .79   |            |

TABLE I—Continued

| No. | Rock and Locality                         | H <sub>2</sub> S | CO <sub>2</sub> | CO    | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|-----|-------------------------------------------|------------------|-----------------|-------|-----------------|----------------|----------------|-------|------------|
|     | <i>Quartz</i>                             |                  |                 |       |                 |                |                |       |            |
|     | Smoky quartz, Branchville, Conn.          | tr.              | 0.07            | 0.00  | 0.00            | 0.00           | tr.            | 0.07  | Wright     |
| 71  | Vein quartz, Iron Co., Utah               | .....            | .11             | .09   | .03             | .53            | .05            | .81   | Chamberlin |
| 83  | Crystals (aqueous origin), North Carolina | tr.              | .03             | tr.   | tr.             | .01            | .03            | .08   | Do         |
| 100 | Auriferous quartz, New South Wales        | 0.01             | .66             | .03   | .04             | .12            | .02            | .88   | Do         |
| 103 | Quartz from pegmatite, Baltimore          | .....            | .09             | .02   | tr.             | .01            | .01            | .13   | Do         |
| 105 | Quartz from lava, Utah                    | tr.              | .12             | .05   | .00             | tr.            | .03            | .20   | Do         |
|     | Average of 6 analyses                     | .....            | .18             | .03   | .01             | .11            | .02            | .35   |            |
|     | <i>Metamorphosed sedimentaries</i>        |                  |                 |       |                 |                |                |       |            |
|     | Pyroxene gneiss, Ceylon (per cent.)       | .....            | 77.72           | 8.06  | 0.56            | 12.49          | 1.16           | 99.99 | Tilden     |
| 27  | Gneiss, Seringapatam (per cent.)          | .....            | 31.62           | 5.36  | .51             | 61.93          | .56            | 99.98 | Do         |
| 28  | Baltimore gneiss, Bryn Mawr, Pa.          | tr.              | .13             | .10   | .14             | 4.32           | .04            | 4.73  | Chamberlin |
| 29  | Baltimore gneiss, Schuylkill River        | .30              | 1.35            | .22   | .11             | 4.02           | .10            | 6.10  | Do         |
| 30  | Wissahickon mica gneiss, Pennsylvania     | tr.              | .19             | .07   | .02             | .65            | .04            | .97   | Do         |
| 31  | Wissahickon gneiss, Schuylkill River      | tr.              | .19             | .08   | .08             | 1.90           | .08            | 2.33  | Do         |
| 43  | Cambrian gneiss, Coatesville, Pa.         | .....            | .26             | .09   | .01             | .37            | .03            | .76   | Do         |
|     | Sillimanite gneiss, Quebec                | SO <sub>2</sub>  | { 2.05          | .09   | .03             | .05            | .07            | 5.05  | Do         |
| 54  | Altered Jurassic shale, Colorado          | 2.76             | carb.           | .15   | .04             | .45            | .04            | .68   | Do         |
| 55  | Garnetiferous gneiss, Quebec              | .11              | .16             | .07   | .02             | .41            | .02            | .79   | Do         |
| 65  | Fine-grained gneiss, Ontario              | SO <sub>2</sub>  | { .68           | ..... | .05             | .....          | .....          | 4.88  | Do         |
| 67  | Feather amphibolite, Ontario              | tr.              | carb.           | .48   | .03             | .32            | .06            | .90   | Do         |
| 68  | Amphibolite, Ontario                      | tr.              | carb.           | .26   | .05             | .01            | .06            | 2.31  | Do         |
| 69  | Rice Rock, Sudbury, Ont.                  | .16              | .47             | .16   | .05             | 2.32           | .06            | 3.22  | Do         |
| 92  | Amphibolite, Chester, Mass.               | .....            | 2.23            | 1.10  | .10             | 2.84           | .13            | 6.40  | Do         |
|     | Average of 13 analyses                    | .57              | .77             | .22   | .05             | 1.52           | .05            | 3.18  |            |

TABLE I—Continued

| No.                              | Rock and Locality                     | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|----------------------------------|---------------------------------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|------------|
| <i>Shales*</i>                   |                                       |                  |                 |      |                 |                |                |       |            |
| 5                                | Kinderhook shale, Burlington, Ia.     | .....            | 9.28            | 0.35 | 0.12            | 0.22           | 0.15           | 10.12 | Chamberlin |
| 6                                | Portage shale, Ithaca, N. Y.          | .....            | 1.47            | .83  | .16             | 1.23           | leak           | 3.69  | Do         |
| 18                               | Hamilton shale, Marysville, Pa.       | tr.              | .41             | .17  | .07             | 1.45           | .40            | 2.50  | Do         |
| 41                               | Hamilton shale, Nashville, Tenn.      | 29.38            | 20.10           | 4.38 | .....           | 37.03          | .....          | 90.89 | Do         |
| 42                               | Oil shale, Platteville, Wis.          | 3.90             | 10.43           | 4.82 | 20.67           | 7.57           | 1.26           | 48.05 | Do         |
|                                  | Average of first 3 analyses.          | .....            | 3.75            | .45  | .11             | .97            | .18            | 5.43  |            |
| <i>Sandstones and quartzites</i> |                                       |                  |                 |      |                 |                |                |       |            |
| 8                                | Potsdam sandstone, Baraboo, Wis.      | .....            | 0.47            | 0.18 | .....           | 0.01           | 0.38           | 1.04  | Chamberlin |
| 12                               | Quartzite schist, Baraboo, Wis.       | .....            | .16             | .07  | .03             | .03            | .06            | .35   | Do         |
| 75                               | Potsdam sandstone, Ablemans, Wis.     | tr.              | .09             | .05  | .02             | .13            | .05            | .34   | Do         |
| 76                               | Same as last, powdered and reheated.  | tr.              | .05             | .07  | .02             | .23            | .08            | .45   | Do         |
| 77                               | Huronian quartzite, Baraboo, Wis.     | tr.              | .11             | .04  | .01             | .24            | .03            | .43   | Do         |
| 78                               | Red Beds, Colorado City.              | tr.              | carb.           | .71  | .07             | .32            | .06            | 1.16  | Do         |
| 80                               | St. Peter sandstone, Minnehaha Falls. | tr.              | .02             | tr.  | .01             | tr.            | .01            | .04   | Do         |
| 81                               | Same as last, powdered and reheated.  | .....            | .03             | .07  | .01             | .17            | .21            | .49   | Do         |
| 82                               | Quartzite, Grenville series, Quebec.  | .23              | .21             | .04  | .01             | .69            | .01            | .59   | Do         |
| 97                               | Micaceous quartzite, Uinta Mountains. | .01              | .57             | .12  | .03             | .03            | .06            | 1.42  | Do         |
| 98                               | Quartzite, Rib Hill, Wis.             | .01              | .62             | .06  | .02             | .17            | .02            | .90   | Do         |
| 99                               | Same as last, granules used.          | tr.              | .86             | .01  | tr.             | .02            | tr.            | .89   | Do         |
|                                  | Average of 12 analyses.               | .02              | .29             | .11  | .02             | .17            | .08            | .69   |            |

\* The two bituminous shales which derived the bulk of their gas from the distillation and decomposition of organic matter are necessarily omitted from the average.

TABLE II  
VARIOUS MINERALS

| No. | Mineral and Locality                 | H <sub>2</sub> S | CO <sub>2</sub> | CO    | H <sub>2</sub> | CH <sub>4</sub> | N <sub>2</sub> | A+He  | Total | Analyst               |
|-----|--------------------------------------|------------------|-----------------|-------|----------------|-----------------|----------------|-------|-------|-----------------------|
|     | Feldspar.....                        | .....            | 1.20            | 0.01  | 0.03           | 0.01            | 0.02           | ..... | 1.27  | Dewar                 |
|     | Celestial graphite.....              | .....            | 6.66            | ..... | .18            | .39             | tr.            | ..... | 7.25  | Do                    |
|     | Graphite, Borrodale.....             | .....            | .95             | .20   | .58            | .68             | .17            | ..... | 2.60  | Do                    |
|     | Chlorite, Zoptan, Moravia.....       | .....            | .33             | 1.33  | 5.84           | .....           | .....          | ..... | 7.50  | Travers               |
|     | Serpentine, Zermatt.....             | .....            | .....           | ..... | 2.08           | .....           | .....          | ..... | 2.58  | Do                    |
|     | Mica, Westchester, Pa.....           | .....            | .42             | .22   | .....          | .....           | .....          | ..... | .64   | Do                    |
|     | Talc, Greiner, Tyrol.....            | .....            | .19             | .11   | .....          | .....           | .....          | ..... | .30   | Do                    |
|     | Feldspar, Peterhead granite.....     | .....            | 3.08            | .55   | .....          | .....           | .....          | ..... | 3.63  | Do                    |
|     | Malacarne.....                       | .....            | 1.55            | ..... | .....          | .....           | .02            | .17   | 1.77  | Kitchin and Winterson |
| 7   | Muscovite, Canada.....               | .....            | 1.26            | .12   | .03            | .04             | .27            | ..... | 1.79  | Chamberlin            |
| 40  | Biotite, Ortonville granite.....     | 0.22             | 12.45           | .23   | .30            | .06             | .21            | ..... | 13.47 | Do                    |
| 48  | Pyroxene crystals, Red Mountain..... | .10              | .69             | .16   | .08            | .01             | .06            | ..... | 1.10  | Do                    |
| 63  | Anorthosite, Quebec.....             | tr.              | 2.36            | .27   | .56            | .02             | .06            | ..... | 3.27  | Do                    |
| 90  | Wollastonite, Lewis Co., N. Y.....   | .....            | 2.37            | .18   | .06            | .02             | .08            | ..... | 2.71  | Do                    |
| 93  | Pitchblende, Beaver Co., Colo.....   | sul.             | carb.           | .24   | .07            | .03             | .27            | .37   | .98   | Do                    |
| 94  | Carnotite.....                       | tr.              | 2.46            | .23   | .05            | .02             | .22            | .04   | 3.02  | Do                    |
| 95  | Greenalite rock, Mesabi.....         | tr.              | .42             | .24   | 5.18           | tr.             | .15            | ..... | 5.99  | Do                    |
| 96  | Grünerite rock, Mesabi.....          | .02              | 1.14            | .26   | 1.39           | .02             | .19            | ..... | 3.02  | Do                    |
| 101 | Beryl, pegmatite, New England.....   | tr.              | .16             | .01   | .31            | .01             | .01            | ..... | .50   | Do                    |
| 102 | Pegmatite with tourmaline.....       | tr.              | .06             | .06   | 1.45           | .05             | .04            | ..... | 1.66  | Do                    |
| 104 | Albite, Yancey Co., N. C.....        | .....            | tr.             | .01   | .04            | .02             | .....          | ..... | .07   | Do                    |
|     | Average of 21 analyses.....          | .02              | 1.88            | .19   | .92            | .06             | .08            | .03   | 3.18  |                       |

that this gas was present and has been included in the figures given for hydrogen.

The unusual amount of gas from the Arva specimen recalls the behavior of the Toluca meteorite,<sup>1</sup> which, at the first attempt, pro-

TABLE III  
STONY METEORITES

| No. | Meteorite                   | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|-----|-----------------------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|------------|
|     | Guernsey, Ohio.....         |                  | 1.80            | 0.13 | 0.06            | 0.95           | 0.05           | 2.99  | Wright     |
|     | Pultusk, Poland.....        |                  | 1.06            | .06  | .06             | .52            | .04            | 1.75  | Do         |
|     | Parnallee, India....        |                  | 2.13            | .04  | .05             | .36            | .04            | 2.63  | Do         |
|     | Weston, Conn.....           |                  | 2.83            | .08  | .04             | .46            | .08            | 3.49  | Do         |
|     | Iowa County, Iowa....       |                  | .88             | .05  | ...             | 1.45           | .12            | 2.50  | Do         |
|     | Kold Bokkeveld.....         |                  | 23.49           | .61  | .82             | .10            | .21            | 25.23 | Do         |
|     | Dhurmsala, India.....       |                  | 1.59            | .03  | .10             | .72            | .03            | 2.51  | Dewar      |
|     | Pultusk, Poland.....        |                  | 2.34            | .19  | .27             | .64            | .09            | 3.54  | Do         |
|     | Mocs.....                   |                  | 1.25            | .07  | .09             | .45            | .07            | 1.94  | Do         |
|     | Orgueil.....                | SO <sub>2</sub>  | 7.40            | 1.14 | .87             | ...            | .33            | 57.87 | Do         |
| 106 | Allegan, Mich.....          | 48.03            | tr.             | .21  | .19             | .01            | .08            | .49   | Chamberlin |
| 107 | Estacado, Texas....         |                  | tr.             | .24  | .25             | .03            | .31            | .84   | Do         |
|     | Average of 12 analyses..... |                  | 4.00            | 3.77 | .24             | .20            | .50            | .09   | 8.80       |

TABLE IV  
IRON METEORITES

| No. | Meteorite                            | H <sub>2</sub> S | CO <sub>2</sub> | CO    | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total | Analyst    |
|-----|--------------------------------------|------------------|-----------------|-------|-----------------|----------------|----------------|-------|------------|
|     | Lenarto.....                         |                  | 0.13            | 0.00  | ...             | 2.44           | 0.28           | 2.85  | Graham     |
|     | Augusta Co., Va.....                 |                  | .31             | 1.21  | ...             | 1.14           | .51            | 3.17  | Mallet     |
|     | Tazewell Co., Tenn....               |                  | .46             | 1.31  | ...             | 1.35           | .05            | 3.17  | Wright     |
|     | Shingle Springs, Cal....             |                  | .13             | .12   | ...             | .67            | .05            | .97   | Do         |
|     | Cross Timbers, Tex....               |                  | .11             | .19   | ...             | .99            | ...            | 1.29  | Do         |
|     | Dickson County, Tex....              |                  | .29             | .34   | ...             | 1.57           | ...            | 2.20  | Do         |
|     | Arva, Hungary.....                   |                  | 5.92            | 31.91 | ...             | 8.57           | .73            | 47.13 | Do         |
|     | Cranbourne, Australia.....           |                  | .04             | 1.13  | 0.16            | 1.63           | .63            | 3.59  | Flight     |
|     | Rowton, Shropshire.....              |                  | .33             | .47   | ...             | 4.96           | .62            | 6.38  | Do         |
| 108 | Toluca, Mexico.....                  |                  | tr.             | 1.32  | .04             | .27            | .10            | 1.85  | Chamberlin |
|     | Average.....                         |                  | .78             | 3.80  | .02             | 2.36           | .30            | 7.26  |            |
|     | Average omitting Arva meteorite..... |                  | .21             | .67   | .02             | 1.67           | .24            | 2.83  |            |

duced 24.42 volumes of gas, owing to the presence of a small quantity of iron rust, but whose pure metal evolved only 1.85 volumes. An average, omitting the Arva, is therefore made.

<sup>1</sup> *Carnegie Publication No. 106*, p. 22.

## AVERAGES OF THE GROUPS

TABLE V  
IGNEOUS ROCKS

| No. | Type of Rock                | No. of Analyses | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-----|-----------------------------|-----------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1   | Basic schists.....          | 2               | 0.00             | 4.06            | 0.19 | 0.05            | 3.44           | 0.13           | 7.87  |
| 2   | Diabases and basalts.....   | 14              | .19              | 3.96            | .44  | .12             | 2.54           | .11            | 7.36  |
| 3   | Gabbros and diorites.....   | 11              | .02              | 2.31            | .13  | .07             | 2.09           | .11            | 4.73  |
| 4   | Granites and gneisses.....  | 19              | .00              | 1.47            | .22  | .05             | 1.36           | .09            | 3.19  |
| 5   | Andesites.....              | 7               | .00              | 1.86            | .18  | .06             | .20            | .09            | 2.39  |
| 6   | Syenites.....               | 4               | .00              | .18             | .07  | .05             | .91            | .04            | 1.25  |
| 7   | Rhyolites.....              | 4               | .00              | .69             | .05  | .02             | .06            | .05            | .87   |
| 8   | Miscellaneous porphyries .. | 2               | .00              | .32             | .06  | .04             | .33            | .04            | .79   |

The general averages bring out the fact that, while rocks of each group may vary considerably among themselves, each group as a whole fits into a logical place in relation to the other groups. The established order appears to be, most gas from those rocks which contain the greatest proportion of ferromagnesian minerals. Though much influenced by other conditions, such as relative age and nature of the igneous mass, the general deduction may be made that the volume of gas obtained from rocks varies, in a rough way, in proportion to the percentage of ferromagnesian minerals present. Diabases, basalts, and basic schists take first rank in the quantity of gas evolved. Next to them appear diorites and gabbros which are also near the basic end, but formed under different conditions. Andesites are out of their place in this list, as they take precedence over granites in the proportion of ferromagnesian minerals, but these andesites were all either of Tertiary or Recent age, whereas most of the granites came from pre-Cambrian formations, and, as the next table will show, ancient igneous rocks yield more gas than modern ones. The rhyolites, which combine a scarcity of basic minerals with Tertiary age, foot the list.

It is to be noted that the rank of a type of rock on the basis of an individual gas does not in all cases correspond to its rank for some other gas, or in respect to total volumes. The andesites tested gave more carbon dioxide than either the granites or the syenites, though both of these types greatly surpassed the andesites in the matter of hydrogen. But this involves another factor: in deep-seated rocks,

hydrogen and carbon dioxide are of about equal importance; in surface flows, carbon dioxide predominates. Though carbon monoxide and methane are somewhat variable, the minor gases generally increase or decrease with the total volumes.

TABLE VI  
ROCKS OF SEDIMENTARY ORIGIN

| Order | Type of Rock              | No. of Analyses | Sulphur gases | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-------|---------------------------|-----------------|---------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1     | Shales (non-bituminous)   | 3               | 0.00          | 3.72            | 0.45 | 0.11            | 0.97           | 0.18           | 5.43  |
| 2     | Metamorphosed sediments   | 13              | .57           | .77             | .22  | .05             | 1.52           | .05            | 3.18  |
| 3     | Sandstones and quartzites | 12              | .02           | .29             | .11  | .02             | .17            | .08            | .69   |

Among sedimentary rocks, sandstones and quartzites yield less gas than shales, while the metamorphic group, comprising both altered shales and sandstones, together with modified limestones, take an intermediate position, though they surpass shales in hydrogen and the sulphur gases.

TABLE VII  
METEORITES

| Order | Type of Meteorite                  | No. of Analyses | Sulphur gases | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-------|------------------------------------|-----------------|---------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1     | Stony . . . . .                    | 12              | 4.00          | 3.77            | 0.24 | 0.20            | 0.50           | 0.09           | 8.80  |
|       | Without SO <sub>2</sub> of Orgueil | 12              | .00           | 3.77            | .24  | .20             | .50            | .09            | 4.80  |
| 2     | Iron . . . . .                     | 10              | .00           | .78             | 3.80 | .02             | 2.36           | .30            | 7.26  |
|       | Neglecting Arva . . . . .          | 9               | .00           | .21             | .67  | .02             | 1.67           | .24            | 2.83  |

A comparison of the two types of meteorites indicates that carbon dioxide is much more important in the gas from stony specimens than in that from the metallic bodies, but that iron meteorites yield several times as much carbon monoxide and hydrogen as do the stones. Sufficient data are not at hand to permit a comparison of the amount of marsh-gas from these two types; nitrogen, however, appears to come in greater volume from the iron meteorites.

#### ANALYSES CLASSIFIED BY THE AGE OF THE ROCKS<sup>1</sup>

In addition to those rocks which could be classed either as Archean or Proterozoic, there were others which could only be called pre-

<sup>1</sup> In this classification of analyses by the age of the rocks, and in the following one based on granularity, only my own analyses have been used.

Cambrian; they are included under the head of Total pre-Cambrian.

TABLE VIII  
IGNEOUS ROCKS

| Order | Age of Rocks           | No. of Analyses | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-------|------------------------|-----------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1     | Archean.....           | 7               | 0.03             | 7.44            | 0.35 | 0.07            | 3.79           | 0.21           | 11.89 |
| 2     | Proterozoic.....       | 8               | .00              | 1.85            | .31  | .07             | 2.08           | .16            | 4.47  |
| 3     | Tertiary.....          | 18              | .00              | 1.20            | .13  | .05             | .53            | .07            | 1.98  |
| 4     | Recent lavas.....      | 5               | .03              | .41             | .07  | .01             | .06            | .02            | .60   |
|       | Total pre-Cambrian.... | 28              | .02              | 2.76            | .23  | .06             | 2.12           | .12            | 5.31  |
|       | Grand total.....       | 51              | .01              | 2.16            | .18  | .05             | 1.36           | .09            | 3.85  |

The rapid and steady decline in the quantity of every gas, in passing down the columns from the Archean through the Proterozoic and Tertiary to Recent lavas, is very striking. These differences may be due to a combination of causes. The older rocks may yield more gas than the recent, owing to metasomatic changes which have been slowly taking place within the rocks. If this be so, the analyses indicate that this process is progressing at an exceedingly slow rate. Or the early magmas may have been more highly charged with gas, some of which has escaped as they were worked over and over and brought to the surface in later times. Both of these processes have probably been operative.

TABLE IX  
SEDIMENTARY AND META-SEDIMENTARY ROCKS

| Order | Age of Rocks     | No. of Analyses | H <sub>2</sub> S<br>SO <sub>2</sub> | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-------|------------------|-----------------|-------------------------------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1     | Proterozoic..... | 17              | 0.45                                | 0.68            | 0.17 | 0.04            | 1.32           | 0.05           | 2.71  |
| 2     | Paleozoic.....   | 10              | .00                                 | 1.34            | .25  | .05             | .41            | .13            | 2.28  |
| 3     | Mesozoic.....    | 1               | .00                                 | carb.           | .15  | .04             | .45            | .04            | .68   |
|       | Total.....       | 28              | .27                                 | .93             | .20  | .04             | .96            | .08            | 2.48  |

Age appears to make less difference in the gas evolved from sedimentary or meta-sedimentary rocks than it does in the case of igneous rocks. All of the Proterozoic specimens were of metamorphic types while only one of the Paleozoic sediments had been metamorphosed. The Mesozoic representative was a Jurassic shale altered by an intru-

sive. The unusual amount of sulphur gas in the Proterozoic list is due to two weathered rocks which contained iron sulphate. However, even with these omitted, the hydrogen sulphide is abnormally high in the rocks of this age. One of the Paleozoic shales was so calcareous as to yield 9.28 volumes of carbon dioxide, which accounts for the large quantity of this gas. The two bituminous shales (analyses 41 and 42) are not included in these averages, since their excessive volume of gas from organic sources would so influence the figures as to disguise some of the characteristics of the other rocks.

## ANALYSES CLASSIFIED BY THE GRANULARITY OF THE ROCKS

TABLE X  
IGNEOUS ROCKS

| Order | Granularity                                | No. of Analyses | H <sub>2</sub> S | CO <sub>2</sub> | CO   | CH <sub>4</sub> | H <sub>2</sub> | N <sub>2</sub> | Total |
|-------|--------------------------------------------|-----------------|------------------|-----------------|------|-----------------|----------------|----------------|-------|
| 1     | Fine-grained .....                         | 22              | 0.02             | 2.75            | 0.31 | 0.06            | 1.68           | 0.12           | 4.94  |
| 2     | Medium-grained .....                       | 18              | .01              | 2.37            | .17  | .05             | 1.41           | .10            | 4.11  |
| 3     | Coarse-grained .....                       | 11              | .01              | .40             | .10  | .04             | 1.20           | .08            | 1.83  |
| 4     | Various porphyries (mostly Tertiary) ..... | 5               | .00              | .41             | .07  | .04             | .22            | .05            | .79   |

From this table it would appear that the fine-grained rocks give off more gas than those of coarser granularity. One of the reasons for this difference probably lies in the fact that metasomatic changes are favored in fine-grained rocks, whose crystals, being smaller, afford more numerous junction-planes between the crystals, through which solutions more readily traverse the rock than in the coarse-grained varieties. Among other changes, hydration and carbonation should alter fine-grained rocks more effectively than coarse-grained ones.

Fineness of grain in igneous rocks usually means that the lava cooled rapidly, and this would hinder the escape of the inclosed gas. But in the process of slow crystallization, such as produces large crystals and coarse texture, much more of the gas would be likely to be crowded out of the growing crystals. However, as a general rule, fine-grained igneous rocks are surface flows, while coarse-texture types were formed at some depth below the surface, and hence a larger proportion of whatever gas was expelled from the rapidly cooling lavas would be more likely to escape altogether than would

be the case with the gas which was excluded from growing crystals in deeper horizons, as in bathylithic intrusions, where final escape was difficult. In this problem of granularity, as in the matter of age, the quantities of gas evolved are probably determined by a combination of complex factors rather than by any single cause.

#### RESULTS AT DIFFERENT TEMPERATURES

The different gases are not all expelled from rock material at the same temperature, nor are they evolved at the same rate. In general, hydrogen sulphide and carbon dioxide are not only the first gases to appear, but they are more rapidly given off than the others. Carbon monoxide follows the dioxide as the temperature is raised, and generally increases in relative importance, as the latter begins to subside, toward the end of the combustion. Hydrogen and marsh-gas are most conspicuous at high temperatures, and hence attain higher percentages in the last half of the gas than in the first half. Nitrogen appears to be disengaged with much difficulty, requiring considerable time at a high temperature.

#### ABSORPTION

Experiments to test the power of gas-absorption by rock material indicated that while a rock powder may take up certain gases while cooling from a high temperature under special conditions, absorption, if it goes on at all at ordinary temperatures, takes place very slowly. However, when rock powders which have apparently been deprived of all their gas were reheated after a sufficient interval of time, there was usually a second evolution of gas. An analysis of the gas from a drill core of Keweenaw diabase from Houghton, Mich., which was kindly furnished by Dr. A. C. Lane, showed 3.88 volumes of gas per volume of rock.<sup>1</sup> After the gas was extracted, the apparently exhausted powder was stored away in a paper bag. Six months later, when reheated, this material yielded 1.92 volumes of gas. From this and other similar experiments it was found that an interval of time partially restores the gas-producing properties of rock powders. For this phenomenon there are two possible explanations. Either, the first heating does not expel all the gas contained in the rock, which, by some sort of diffusion or molecular rearrangement, gradually pre-

<sup>1</sup> Analysis No. 85.

pare itself to come off when again heated; or else the rock powder absorbs gases from the atmosphere. To exclude atmospheric absorption this Keweenaw diabase powder, which originally gave 3.88 volumes, and after six months 1.92 volumes, was heated a third time (a week later) with the evolution of very little gas. This powder, after cooling in the vacuum, was taken out of the combustion tube and immediately placed in a flask filled with freshly distilled water. A stopper being fitted into the flask, it was allowed to stand for three days. At the end of this time, the water was poured off, the powder quickly, but thoroughly, dried, and put into the combustion tube. When heated, this powder gave off .79 volumes of gas, of which carbon dioxide constituted 67 per cent. This carbon dioxide could not have come from the air, but must have existed within the rock material and must have withstood three successive heatings in the combustion tube. This experiment favors the conclusion that the gas which is obtained from a rock powder by a second or third heating after a period of time, is due, not so much to a process of selective absorption from the atmosphere, as to changes which have been slowly taking place within the powder itself.

#### STATES IN WHICH THE GASES EXIST IN ROCKS

In order to explain the immediate source of the gases obtained by heating rock material in vacuo, three different hypotheses naturally present themselves. The simplest of these is to suppose the gases to exist in minute cavities or pores, having been entrapped within the rock during the process of solidification. This supposition is suggested and supported by the observation that microscopic slides of some minerals, notably quartz and topaz, reveal numerous small gas-bubbles. But while there is evidence that some gas is thus held in cavities, there is equally strong evidence to show that the greater part of it cannot be attributed to this source.

To escape the difficulties encountered by the first hypothesis, appeal is made to the imperfectly understood property of some of the elements to "occlude," or dissolve within their mass, certain gases. It is remembered that under the proper conditions palladium will occlude 900 times its own volume of hydrogen, and that the same gas is also absorbed, in lesser degree, by other metals, particularly plati-

num and iron, while silver has a similar affinity for oxygen. This principle applied to igneous rocks as a hypothetical source of their gases becomes at once a more difficult proposition to prove or disprove.

The third hypothesis, more conservative than either of the others, assumes that these gases do not exist in the rocks in the uncombined, or gaseous state, but are produced in the combustion-tube by chemical reactions at high temperature.

#### GAS IN CAVITIES

The studies of Brewster, Davy, Sorby, Hartley, and others, have established the presence of gas, generally carbon dioxide, though sometimes nitrogen, in the minute cavities of certain crystals. But while microscopic investigations have indicated that carbon dioxide constitutes more than 90 per cent. of the gaseous matter inclosed in these cavities, and hydrogen is found in traces only, the latter gas is the most important constituent of the mixture derived from rocks by heat. In addition to this, the observation that those rocks which are not known to contain many gas cavities produced several times as much gas as the cavernous quartzes, also suggested that the bulk of the gas, at least, could not be attributed to inclosure in cavities. Moreover, basic rocks were found to be more productive than acidic, whereas it had generally been supposed that the latter, owing to their greater viscosity, should entrap more gas and vapor than the more fluid basic lavas.

The suspicion that the gas did not come from cavities in any large degree was strengthened by the observation that the composition of the gas varied according to the temperature to which the rock powder was heated. If from cavities, the liberation of the gas should commence with a slight rise of temperature, and should continue more or less steadily, as the heat increased, until the expansive force of the gas had burst open most of the pores. Since all gases expand equally, one should burst its confines as soon as another, and a sample of gas obtained at any given temperature should not differ very widely in composition from that evolved at any other.

These and other considerations led me to try a series of experiments which should show how much gas actually could be obtained from the opening of cavities alone. For this purpose a crusher was devised,

which was capable of pulverizing a rock specimen in a complete vacuum. Any gas liberated could then be pumped off and analyzed. Two specimens of basalt, one from the Faroë Islands and the other from Hawaii, gave little or no gas. Vein quartz from Iron County, Utah, gave no trace of gas. Being desirous of finding some specimen which would yield gas when crushed in this manner, I procured some crystals of cavernous quartz from Porretta, Italy, in which several of the cavities exceeded a millimeter in diameter. These, when crushed, yielded carbon dioxide amounting to only .03 of the volume of the quartz. An analysis showed also a little methane and some nitrogen, but the amount of gas available was too small for the determination to be of any value. The result of this last test agrees with the microscopic studies of the early investigators. Carbon dioxide exists in the cavities of quartz, but its volume, compared with the volume of inclosing mineral, is small.

#### GASES DUE TO CHEMICAL REACTIONS

We may note very briefly the possible sources of gas from high-temperature reactions between the non-gaseous constituents of the rocks.

Hydrogen may be produced at temperatures above 500° through the decomposition of steam by a ferrous compound.

Carbon dioxide is liberated when an ordinary carbonate is heated sufficiently, and hence if the rock specimen be slightly carbonated, gas will be derived from this source and will embarrass the determination of the free gas.

Carbon monoxide is formed from carbon dioxide when that gas is heated in the presence of iron in the ferrous condition, and also to a lesser degree when heated with free hydrogen.

Possible sources for methane are carbides, the decomposition of organic matter, and the reaction between carbon monoxide and free hydrogen which gives marsh-gas and water.

Nitrogen and the sulphur gases may be attributed in part to nitrides, sulphides, and basic sulphates.

Many of these chemical reactions actually took place in the combustion tube during the process of extracting the gas from the rock material, and in some cases the larger part of the gas doubtless was

produced in this way from the non-gaseous constituents of the rocks. But these reactions were, in some instances at least, quantitatively inadequate to produce all the gas obtained. Quantitative experiments upon quartz and beryl indicated a considerable excess of hydrogen over what could possibly be produced from reactions involving the entire weight of iron salts in these minerals. Particularly striking was the case of a beryl from New England which expelled 150 times as much hydrogen as could be assigned to the interaction of steam and ferrous oxide under the most generous assumptions, and 37 times the maximum quantity possible from the total weight of iron in the material if it all occurred either as pyrite or in the metallic state.

#### OCCLUDED GASES

Such gas as was not held mechanically entrapped within cavities, nor originated from chemical reactions within the combustion tube, is assigned to that imperfectly understood phenomenon to which Graham gave the name *occlusion*. Because the possibilities of obtaining gas from hydration and carbonation are much reduced in the case of freshly fallen meteorites, these bodies in some respects furnish the best conditions for studying the truly occluded gases. To obtain fresh material which had not been subject to hydration and carbonation, a fragment from the Allegan meteorite was obtained from the National Museum. This stone, which was gathered up still hot, within five minutes of its fall, and has not been subjected to outdoor exposure, yielded somewhat more than half of its own volume of gas. Material from the interior of other meteorites yielded even more gas.

In the case of rocks, the amount of occluded gases may be actually greater than that indicated by demonstrating the inadequacy of the other modes of holding gas to account for the total quantity extracted in the laboratory. But a determination of the exact proportion of occluded gas in these cases would be difficult. In general, argon and helium, which do not enter into chemical combination, together with at least as much of the other gases as can be shown not to have been produced by chemical reactions, or the bursting of inclosing walls, are to be attributed to occlusion, or to some form of diffusion not distinguishable from occlusion.

## SIGNIFICANCE OF THE THREEFOLD STATE

While chemical reactions and the phenomena of occlusion imply that gas exists in the interior of the earth, the presence of gas inclosed in cavities, under great pressure, adds the further implication that the gas often exceeded the point of saturation of the magma, at least at the stage of solidification. Cavity gases are most abundant in minerals of poorly developed cleavage, pointing perhaps toward a strong tendency to escape along cleavage planes during, or after, crystallization. While most commonly observed in non-cleavable quartz, the gas inclusions in that mineral may owe their abundance to the fact that quartz is generally the last mineral to crystallize out of a magma, and hence such absorbed gases as did not enter into the other crystals would become concentrated in the siliceous residue, and might supersaturate it. It is probably this freely moving gas above the point of saturation which contributes most to the mobility of lavas. Dissolved gases and vapors, while favoring fluidity, would seem to be relatively less effective. However, gases mechanically entrapped in crystalline rocks are quantitatively not very prominent, suggesting that perhaps the theory of liquidity due to gas is overworked. But, on the other hand, it is true that as a lava cooled down to the point where the last mineral crystallized, its gas-solvent powers would be increasing, allowing some of the gas to pass into solution. At the same time, free gas would be occluded by the growing crystals. Experiments upon the re-absorption of gas by exhausted rock powder indicate that a portion of the gas unites chemically as the heat diminishes. Because of these processes, liquid lavas may be supplied with free gas, though the solidified rocks retain but little gas in this condition.

## WATER AND HYDROGEN

The reversible reactions involving hydrogen, water, and iron compounds, which cause uncertainties in the extraction of gases by heat, are also operative within the earth. In the laboratory, when either ferrous salts and water, or ferric compounds and hydrogen, are heated in tubes without the removal of the products, reversible reactions set in until a condition of equilibrium is established. Hydrogen and water, ferrous and ferric salts, are all present in a state of balance. In the interior of the earth, the heated, though solid rocks

should, it would seem, behave similarly, though hindered by the slowness of diffusion. Nor should liquid magmas constitute any exception to the law. Both hydrogen and water gas, theoretically, should be present in liquid magmas and heated solid rocks.

For reasons which cannot be discussed here, chemical equilibrium favors the formation of ferrous salts and water, as the temperature increases. Because of this, there is much reason to suppose that, at the depths where lavas originate, hydrogen and oxygen exist combined as water, since up to temperatures of 2,000° C. the dissociation of water takes place only to a limited extent. If a state of equilibrium between hydrogen, water, and the iron compounds were established in the heated interior where a magma originated, as soon as it commenced its way upward and began to lose heat, the condition of equilibrium would be destroyed. With the falling temperature, the tendency to re-establish equilibrium would favor the formation of that system which was produced with the liberation of heat, i. e., magnetic oxide and free hydrogen. In ascending lavas, which are losing heat, the tendency, therefore, is to produce hydrogen and magnetite, or ferrous-ferric compounds. This is doubtless an important source for the hydrogen which is so copiously exhaled during a volcanic eruption. At the same time this process accounts for the widespread occurrence of magnetite in igneous rocks.

In general, these reversible reactions tend to show that it is but a short step from hydrogen to water, and from carbon dioxide to monoxide, and vice versa, and that all of these must occur within the earth owing to the process tending toward equilibrium. Whether hydrogen, in a particular case, occurs in the magmas in the free state, or in the form of water gas, therefore becomes relatively unimportant. Because of this variation of state, the problem becomes more complex and broader in scope. For the most part, these water gases are to be regarded as truly magmatic, and not derived from surface waters penetrating to the liquid lavas. But this is a complex question and cannot be touched here. These water gases are here put forward as essential factors in the evolution of the magmas from the original planetary matter.

The reactions working toward equilibrium are able to supply hydrogen and carbon monoxide under conditions favorable to their

absorption and retention, even if they were not originally present as occluded gases. The sources of the gases obtained from rocks are so complex that it is difficult to determine how much is to be assigned to each. Because of the penetration of surface waters containing carbonic acid in solution, throughout the accessible rocks of the earth's exterior, it is likely that, in many cases, the bulk of the gas obtained by heating powders in vacuo has been derived from acquired water and carbonated compounds. But in fresh meteorites, which presumably have not been subjected to action of this sort, occlusion is relatively more important.

From the constitution of meteorites, some of the principles of early terrestrial evolution may, perhaps, be inferred, though the growth of the earth was probably not quite analogous, in all respects, to the formation of the meteorites. Whether we take the meteoritic material to represent the heavier part of the original matter of the solar system, or the stellar system, as a whole, matters little in the geologic problem. If, in truth, the unoxidized, heterogeneously aggregated material of meteorites be typical of the original heavy material of the earth, it becomes evident that, in the case of our planet, other factors have been at work which are not operative in the bodies of which the meteorites are supposed to be fragments. These visitors from space are characterized by such minerals as cohenite,  $(\text{Fe, Ni, Co})_3\text{C}$ , lawrencite,  $\text{FeCl}_2$ , oldhamite,  $\text{CaS}_2$ , and schreibersite,  $(\text{Fe, Ni, Co})_3\text{P}$ , which, next to nickel-iron, is the most widely distributed constituent of iron meteorites,<sup>1</sup> though of less importance in the stony specimens. Such compounds imply an absence of both free oxygen and water in notable quantities. Of like import is the absence of hydrated minerals, such as micas and amphiboles. Water and an oxygenated atmosphere appear to be the agents which are lacking in the bodies from which the meteorites were derived, but which have been the operative factors in working over the outer portion of the earth.

But the original source of the earth's atmosphere and hydrosphere is taken to be gas occluded, or absorbed, in the primitive meteoritic material. These original gases, escaping, furnished both atmosphere and hydrosphere when the earth became of sufficient size to retain

<sup>1</sup> Farrington, *Jour. of Geol.*, Vol. IX, pp. 405-7, 525, 526.

them. A self-regulating system was inaugurated. In the early stages of the hydrosphere, when growth by infalling planetesimals was rapid, much water was buried within the fragmental crust. This material, worked over by volcanic activity, brought to the surface and subjected to weathering and erosion, and buried beneath more material, has undergone assortment and alteration until the accessible rocks at the present time are very different from the meteoritic matter. Since the earth attained its growth and the infall of planetesimals slackened, much less water has penetrated to great depths below the surface. Post-Archean sedimentaries have not yet reached thicknesses sufficient to carry inclosed water down to the depths from which the lavas arise. Deep mines indicate that fractures and fissures do not convey water down to very great depths at the present time. If water does not penetrate so rapidly now, and hydration and carbonation are less effective, it is also probably true that subsiding vulcanism brings less gas to the surface.

It is essentially a system of balance. At the same time that water is being buried with sediment, its elements, hydrogen and oxygen, the latter in the form of the oxides of carbon, are exhaled from the earth's interior through volcanic outlets. But the system here suggested is very different from the postulated limited cycle of underground water which, following Daubrée's famous experiment,<sup>1</sup> has crept into geologic literature as the origin of volcanic vapors and the *modus operandi* of vulcanism. Instead of surface waters following cracks and fissures down to the hot lavas there to be absorbed, the water already is present, and is a part of the rocks and magmas in the interior, whether actually combined as water, or as its elements held in solution, or chemically united in other compounds. These gaseous elements form an integral part in the magmas, having been vital factors in their development from the primitive planetary matter. That this process of reworking has gone on to considerable depths, if we are to start with typical material, is evidenced by the fact that the deep-seated plutonic rocks are characterized by micas and other hydrous minerals, while mineral species of the meteoritic type are absent.<sup>2</sup>

<sup>1</sup> Daubrée, *Études synthétiques de géologie expérimentale*, Tome 1, pp. 236-46.

<sup>2</sup> This statement should perhaps be qualified. The basalt at Ovifak, Greenland, contains iron strongly resembling the meteoric metal, in which the minerals cohenite,

The more restrictive phase of the problem of water will be discussed under the head of vulcanism.

#### VULCANISM

In the actual dynamics of vulcanism, provided the gases are original in the magmas, the state in which they occur is not of vital importance, except in so far as it determines the conditions under which the gases become free, from occluded or chemical bonds, to perform their part in the mobility of lavas, in the explosions which sometimes accompany eruptions, and in the phenomena of fumaroles and volcanic vents. The distinction between cavity, occluded, and chemically united gas, which is made in the case of solid igneous rocks, cannot be extended to the liquid lavas. In the liquid lava the gas may be supposed to be imprisoned mechanically, or else to form a part of the magmatic solution. On the solidification of the mass, the gas, formerly existing in the free state, may enter chemical combinations at the lower temperature, may be occluded by the solid rock, or may become entrapped within the minerals last to crystallize. So, too, it is possible that some of the gas dissolved in the magma may, because of cooling and crystallization of adjacent portions of the solution, reach a super-saturated condition and appear in the solid rock also as gas inclusions. Otherwise, it would pass into the solid rock occluded or chemically combined. The condition of the gases examined in the laboratory need not, necessarily, correspond to a particular state of occurrence in the lava before crystallization.

Gases mechanically distributed throughout the lava would always be an operative factor in vulcanism, while such gases as were chemically combined in the solution would, presumably, only become free, and hence fully operative, upon the lowering of the temperature and the relief of pressure,<sup>1</sup> and probably but partially then. Since vapors and gases in the free state are the cause of volcanic explosions, they can be traced as far down in the conduits as explosions occur. From the nature of these explosions, which appear to be due to the accumulation of gas, it is probable that the gases which have been recognized as lawrencite, and doubtfully schreibersite have been recognized. The occurrence of this terrestrial iron would indicate that material of this sort still occurs at points within the outer part of the earth.

<sup>1</sup> A falling temperature favors the liberation of hydrogen from water by ferrous compounds (see p. 553), while carbonates are most easily decomposed at low pressures.

lation of vapor gradually working upward until suddenly able to relieve itself, it is fair to suppose that aqueous vapor and the auxiliary gases are present in the free state at still greater depths.

It has been the observation of those who have studied volcanic eruptions that water vapor is by far the most abundant of the gaseous products of volcanoes. Water is also the principal compound of the element hydrogen, which is quantitatively the most important gas obtained by heating igneous rocks *in vacuo*. According to one of the common theories of vulcanism, it is water, circulating underground and necessarily dissolving and absorbing mineral and gaseous material, which penetrates to the lavas and gives to them their supply of vapor and gases. Water, then, is a critical element in the theories of vulcanism, and likely to be a decisive factor upon the basis of which many of these theories may stand or fall. It is, therefore, of great importance to know whether the aqueous vapor, which is so copiously exhaled from volcanic vents and plays such a rôle in vulcanism, is derived originally from the magmas, or is merely underground water which has been incorporated by the lava in its journey upward. A decision of this question will carry with it the solution of the allied question concerning the ultimate source of the other gases, and also throw much light upon some of the more comprehensive theories of vulcanism.

Appealing to the fact that chlorine, in the form of hydrochloric acid and volatilized chlorides, is one of the products of volcanoes, one of the standard hypotheses attributes the cause of vulcanism to the penetration of sea water to the heated interior. If this were so, isolated volcanoes far out at sea would be expected to yield much more chlorine than those on the continents. But the Hawaiian volcanoes exhale comparatively little chlorine or sublimed chlorides. It has been claimed that rain water, sinking into the cone, would have sufficient head to exclude the sea water from the neighborhood of the hot lava. Rain, however, falls upon but a small part of the whole cone, whose greater portion is under the sea. It would seem that if rain water, falling upon a cone built up from the ocean bottom, is able, by means of its head, to keep out the sea water which covers the lower slopes, the same amount of water precipitated upon a continental volcano would be even more efficient in preventing the general underground

water from coming in contact with the lava in the conduit. Whatever may be the reason for the small amount of chlorine given off by the volcanoes of Hawaii, sea water does not reach the heated lavas in sufficient quantities to affect them appreciably.

On account of the pressure exceeding the crushing strength of the rock, pores and crevices cannot exist at depths greater than 30,000 feet according to the most generous estimate,<sup>1</sup> and it is probable that continuous cracks cease much short of this. Beyond this extreme figure, meteoric waters cannot be regarded as of any quantitative importance, on account of the extreme slowness of diffusion through solid bodies not containing minute fractures. Liquid carbon dioxide, still existing under great pressure in sand grains of pre-Cambrian age, is a concrete example of this slowness. While, theoretically, water may extend downward to the limit of the zone of fracture, the testimony of deep mining appears to show that meteoric waters grow relatively scant, as a rule, below the uppermost 1,500 to 1,800 feet of the earth's crust.<sup>2</sup> This shallowness of meteoric water increases the difficulties encountered by the hypothesis that the lava beds are supplied from this source, since they rise from far greater depths and only the upper portions of their conduits would be exposed to these waters. It is in this portion of the zone of fracture that Daubrée's much-quoted experiment upon the Strasbourg sandstone<sup>3</sup> finds its application, if anywhere, since numerous capillary pores with plenty of water are requisites for the operation of this principle. This famous experiment demonstrated that, owing to its force of capillarity, boiling water will pass through a disk of sandstone, 2 centimeters in thickness, against a slight steam-pressure on the other side. But it was only necessary for the steam-pressure to reach 685 millimeters, or nine-tenths of an atmosphere, in order to prevent any more water from passing through the sandstone. It is a long jump from this trivial capillary force, equal to less than one atmosphere of steam pressure, to the great pressures which would have to be overcome in the depths of the earth's crust in order to reach the hot lavas, even

<sup>1</sup> Hoskins, *16th Ann. Rept.*, U. S. Geol. Surv., p. 853.

<sup>2</sup> Kemp, *Economic Geol.*, Vol. II (1907), p. 3; Finch, *Proc. Col. Sci. Soc.*, Vol. VII (1904), pp. 193-252.

<sup>3</sup> Daubrée, *Études synthétiques*, Tome 1, pp. 236-46.

though it be allowed that the water vapor, if it came in contact with the lava, would be absorbed. Capillary force seems quantitatively inadequate.

To reach the critical pressure of water due to the hydrostatic column, it is necessary to penetrate the earth to a depth of about 6,900 feet. At depths less than this, water passing into the vaporous condition, in the neighborhood of hot volcanic conduits, at temperatures below the critical point, should leave behind more or less of the matter held by it in solution, since the condensation, and hence molecular attraction of the vapor for solutes, is less than that of the water. Thus even if vapor from underground waters should enter the lavas, as Daubrée has suggested, in the outer 6,900 feet of the earth's crust, much of the chlorides, sulphates, carbonates, and silicates, dissolved in the water, would have been left behind. At depths between 6,900 feet and 25,000 feet, beyond which water cannot penetrate, owing to the closure of all pores by the pressure of superincumbent rock, mineral matter dissolved in the water would probably still remain in solution when the liquid passed into the gaseous state at the critical temperature, since the density of the gas is equal to, or greater than, that of the liquid.

The lava, being under considerable pressure, may be supposed to occupy all the cracks and crevices in the adjacent rocks, except those of capillary dimensions. If, therefore, in the passage of underground water into vapor, preparatory to entering lavas in the outer 6,900 feet of the earth's crust, much of the dissolved mineral matter be deposited in the minute pores leading to the lava, they should quickly become sealed, preventing any further access, even of water, to the lava. To test this principle experimentally, a cylinder of medium-grained Potsdam sandstone from Wisconsin, 40 millimeters in diameter and 28 millimeters in thickness, was soldered into a short piece of iron piping, fitted at one end with an elbow to serve as a receptacle for water, and at the other with a cork and a condenser. When ready, the receptacle was filled with Lake Michigan water and a Bunsen burner was placed so as to heat the sandstone cylinder within the iron tube. One side of the sandstone was thus kept at a temperature slightly above  $100^{\circ}$ , while the other face, in contact with the water, remained just at the boiling-point. Water was found to

penetrate the porous cylinder readily, evaporating and leaving its dissolved material within the mass of the sandstone, and escaping as steam on the farther side. The rate at which the water passed through the sandstone at the outset was not determined, but after 5 liters of lake water had been used, it was found that 129 cubic centimeters traversed the rock and were condensed in one hour. The rate slowly fell as the experiment progressed. While the thirteenth liter was being used, only 73 cubic centimeters passed through the sandstone per hour. It was evident that the pores were becoming clogged, but to complete the experiment with Lake Michigan water, which contains only 150 parts of solid matter per million, would have required too much time. To hasten the process, a saturated solution of calcium sulphate was substituted. This soon caused a marked slackening of the passage of water through the rock, and doubtless would have sealed the pores completely, if allowed sufficient time.

From this experiment, it appears certain that water, evaporating in the pore spaces of a rock and escaping as steam, will leave behind whatever material is in solution, until the crevices become clogged and the penetration of water ceases. This principle may be applied to the outer 6,900 feet of the earth's crust; in the superficial portion of this zone it should be very effective, since the conditions more nearly approach those of the experiment; in the lower portion of this belt, as 6,900 feet and the critical pressure (as well as temperature in the neighborhood of hot volcanic pipes) is approached, the density, and hence the solvent powers, of the water vapor approach those of the liquid. Toward the critical point of water, therefore, the application of this principle becomes more uncertain, but it would seem to be operative also at these depths, though more and more slowly as the critical point is neared.

It might be objected that the passage of water into vapor, involving the latent heat of steam, would keep the adjacent rocks cool and cause the deposition to take place at the very contact where the hot lava could fuse, and dissolve, the precipitated salts. But it is very doubtful whether the vaporization of such a small quantity of water, taking place with the slowness imposed upon it by the minuteness of the capillary pores, would keep the contact rocks at a temperature below 365°. The gap between 365° and 1,100° is too great for there

not to be a space, if of a few inches only, at an intermediate temperature. It is also to be remembered that the latent heat of steam diminishes with the pressure until, at the critical point, it becomes zero. The testimony of the country rocks through which a volcanic conduit has passed is that metamorphism has usually progressed to some distance from the contact of igneous intrusion. In a long-established volcano, where the rocks surrounding the conduit have been heated to high temperatures, the deposition of the solutes from any penetrating water should have sealed the capillary tubes and fissures at a distance from the lava such that the latter cannot absorb them and keep the waterway open. Kemp has stated in a recent paper<sup>1</sup> that at the contacts with eruptives, limestone rocks, instead of being porous, are prevailingly dense and compact, and often very hard to drill, as if due to deposition within their interstices. However, the author assigned this supposed deposition to magmatic waters from the intrusion. This brings up a widely established view that magmas, instead of absorbing water from the intruded rocks, give it off, depositing matter in solution to form veins in the zone of fracture.

To quote Van Hise:<sup>2</sup>

In the belt of cementation, in consequence of the porosity of that zone, the material of the magma, both by direct injection and by transmission through water, may profoundly affect the average chemical composition of the intruded rock for great distances from the intrusive mass.

Geikie cites a case in Bohemia, where certain Senonian marls, invaded by a mass of Tertiary dolerite, begin to get darker in color and harder in texture at a distance of 800 meters from the contact, while, as the intrusive mass is approached, the interstratified beds of sandstone have been indurated to the compactness of quartzite.<sup>3</sup>

But considering only meteoric waters at depths greater than 6,900 feet, where water remains liquid up to the critical temperature, it is less probable that the pore spaces will be filled up in this manner. Nor does it seem likely that Daubrée's theory that water may penetrate rocks against a steam-pressure can operate at these depths,

<sup>1</sup> Kemp, *Economic Geol.*, Vol. II, p. 11.

<sup>2</sup> Van Hise, *Monograph 47*, U. S. Geol. Surv., p. 714.

<sup>3</sup> Hibschi, cited by Geikie, *Textbook of Geology*, Vol. II, p. 774.

since that principle is dependent upon a marked difference between the capillarity of water and of steam, while at the critical point, the density of water-gas being the same as that of water, this force should be absent. The problem then becomes a question of equilibrium between the hydrostatic column of water and that of the lava, in which the pressure of the lava at a depth of 7,000 feet should be in the neighborhood of 2.7 times that of the water, though this preponderance steadily diminishes as the water-gas becomes condensed, with increasing depth, at a rate higher than lava. Whether under these conditions lava can absorb water-gas, is an open question.

Water can only penetrate from 25,000 to 30,000 feet below the surface on account of the closure of all crevices by pressure. But on the assumption that the temperature gradient in the outer part of the earth's crust is  $1^{\circ}$  C. for each 100 feet of descent (which is probably too high) the critical temperature will not be reached, except in the neighborhood of volcanic intrusions, until at a depth of about 36,000 feet. Hence, over the greater part of the earth, water will remain in the liquid state as far down as fractures and fissures will allow it to seep, and no appeal can be made to the more rapid and potent gaseous diffusion to carry it beyond 30,000 feet. But because of their heat, lavas must originate at much greater depths below the surface, and hence far beyond the reach of surface waters, which can only come in contact with them, and only doubtfully then, in a very limited portion of the throat of the volcano.

These considerations seem to indicate that, for the most part, the volcanic gases and vapors have not been supplied to the lavas by ground waters, but are original constituents of the magmas. Doubtless at the beginning of an eruption, following a period of quiescence, much of the steam merely comes from such rain water as may have accumulated in the crater and upper part of the cone, but this does not account for the gaseous emanations from the lava itself, nor from those volcanoes, such as Stromboli, and the well-known Solfatara near Naples, which maintain a mild form of eruption for long periods. Such meteoric water could contribute to the volcanic gases little except some dissolved air, together with a trace of carbon dioxide, and perhaps hydrogen from chemical action. Such soluble salts as this water might dissolve from the crater walls were brought up from the

interior in the first place (making some allowance, however, for weathering), and so have little bearing on the case.

The hypothesis that the gases and vapors are originally from the magmas is greatly strengthened by the volcanic activity in the moon, if, as is rather generally believed, the great pits on the surface of the moon are craters produced by volcanic explosions; if not, of course the argument does not hold. The gases and vapors which caused the tremendous outbursts cannot be ascribed to the penetration of surface waters and gases, for the moon has neither appreciable atmosphere nor hydrosphere, and, according to Stoney's doctrine, never could have held either, owing to its feeble gravitative control. Such gases as are implied by these explosions must be supposed to have arisen from within the interior of the moon. The extent of this explosive lunar vulcanism, in the absence of any appreciable atmosphere or hydrosphere, furnishes a strong argument against the belief that surface waters and atmospheric gases are essential factors in terrestrial vulcanism.

Thus far evidence of a negative nature has been brought forward to show the difficulties in the way of thinking that surface waters play a prominent rôle in volcanic phenomena. But more positive evidence can be presented to support the view that the hydrogen and water in the deep-seated rocks are truly magmatic. Micas are prominent constituents of the plutonic rocks. The immense granitic bathyliths, which were probably formed beyond the reach of ground waters, are characterized by this group of minerals. In fact, micas are more abundant in the deep-seated rocks than in the surface lavas of similar composition. Yet all micas contain hydrogen (or hydroxyl) and yield water upon ignition. This varies with the mineral species and locality, ranging up to 4 or 5 per cent. If these micas in the massive intrusions are primary minerals, as they seem to be, and were out of the reach of ground waters until long after they were crystallized, there appears no other alternative than to consider this hydrogen as inherent in the magma itself. The general petrological principle that plutonic rocks are micaceous and hornblendic, while their more superficial equivalents are more frequently characterized by pyroxenes which are less hydrous, may point toward the suggestion that the magmas originally contain considerable water or the elements which

can produce it, but as they approach the surface much of the hydrogen and water vapor escapes and pyroxene minerals crystallize instead of these hydrous micas.

All of these facts and deductions lead to the general conclusion that our surface waters have been derived from the interior of the earth, and oppose the idea that to explain the presence of hydrogen, or water, in magmas and rocks, we have merely to appeal to the penetration of surface waters. The meteoric waters are limited to their superficial place and function, both in the evolution of magmas and in vulcanism; an ultimate source is found for these waters; and a steady supply of water and gases is furnished to the earth to offset the loss of vapor into space, and thus contributes to the globe one of the factors necessary to a long period of habitability for living organisms.

#### VOLCANIC GASES

The gases which escape from fumarolic vents are in many respects similar to those obtained by heating igneous rocks *in vacuo*, but with the addition of oxygen and vapors of chlorides, fluorides, boric acid, and other high-temperature volatilizations. Though nitrogen is much more conspicuous in the analyses of volcanic gases than in those from rocks, this is doubtless due, in the main, to a mixture with atmospheric air. However, the greater heat of the volcano would also favor a higher proportion of nitrogen, as shown by my experiment. Much of the oxygen also is probably from the air. But an analysis of gas escaping from a stream of lava flowing on the sea bottom at Santorin gave Fouqué: oxygen, 21.11 per cent.; nitrogen, 21.90 per cent.; and hydrogen, 56.70 per cent.<sup>1</sup> This would suggest that the dissociation of water also contributes free oxygen.

Fouqué's studies at Santorin confirm the law of variation in composition of volcanic gases, first established by Sainte-Claire Deville,<sup>2</sup> namely, that the nature of the gas evolved depends upon the phase of volcanic activity. Hydrochloric acid, with free chlorine and fluorine, is given off only from the hottest fumaroles where the heat is sufficient to liberate these gases from chlorides and fluorides. At less active vents, sulphur dioxide is the most noticeable of the corrosive gases, while the cooler fumaroles exhale chiefly hydrogen sulphide, carbon

<sup>1</sup> Fouqué, *Santorin et ses éruptions*, p. 230.

<sup>2</sup> Sainte-Claire Deville, *Ann. de chim. et phys.*, 52 (1858), p. 60.

dioxide, and nitrogen. Carbon dioxide and nitrogen escape from all the fumaroles. Fouqué found that the relative importance of hydrogen increased with rise of temperature, and that his marsh-gas (which, owing to an imperfection in the method of analysis in 1867, may have been carbon monoxide, or a mixture of carbon monoxide and marsh-gas) diminished as the activity increased. These observations are entirely in accord with the results of my differential temperature experiments with rock powders. Hydrogen sulphide and carbon dioxide are the gases expelled from the rocks at the lowest temperatures; carbon monoxide and marsh-gas appear at intermediate temperatures, while hydrogen is most prominent when the heat is carried to bright redness. Nitrogen is most abundantly liberated at red heat; hence the presence of that gas at the cooler vents and fissures is chiefly due to atmospheric air.

While carbon dioxide escapes from all fumaroles in greater or less degree, it is at those vents whose activity has subsided beyond the point where hydrogen and the noxious gases are evolved that this gas is most conspicuous. For this reason, carbon dioxide has come to be regarded as marking the dying-out of the volcanic activity. A source for carbon dioxide after the disappearance of the other gases has been sought in the neighboring limestone formations, either from baking or from the chemical action of halogen or sulphur acids. The obvious difficulty confronting this conception is that limestone is not always present to furnish carbon dioxide. Experiments show that below 400° C. carbon dioxide is the principal gas evolved from rock material, and as the lava solidifying in the crater, or conduit, has not lost all its gas, it is only a part of the natural sequence of events that the escape of carbonic anhydride from the cooling lavas should continue for some time after the volcano has settled into quiescence. Some of this carbon dioxide doubtless also comes from previous lavas which, warmed again by the fresh lava, give up some of the carbon dioxide which my experiments show them to contain.

#### GENERAL RELATIONS

##### RELATIVE TO THE HYPOTHESIS OF A MOLTEN EARTH

These studies show that, within the range of temperature employed, heat causes the expulsion of gases in whatever form they are held, and

that the greater the degree of heat the more quickly and completely the gases are given off. There is reason to believe that this principle applies to the molten state as well as to the solid condition. If it be applicable to liquid lavas, it would favor the belief that a molten globe would have boiled out most of its gaseous matter before solidifying. Gases near the surface should escape rapidly. It might, perhaps, on first thought, be held that, while much of the gas in the outer portion would be lost, that existing in the central part of the sphere would be retained and slowly recharge the peripheral portion after a crust had formed and prevented further escape; but the molten globe, by hypothesis, grew up gradually, and essentially every part was once superficial. Even today, in an essentially solid earth, there are movements of lava that bring up gases from unknown depths, and it is reasonable to suppose that the molten sphere was stirred up by still more effective convection currents which facilitated the expulsion of gases and vapors, and that almost all of the gaseous material of the globe would have been boiled out before solidification set in.

The complete validity of this view depends much upon the fate of the gases after they have reached the surface. If they were retained in the form of a dense atmosphere, a condition of pressure-equilibrium might be established between the atmosphere and the gases in the liquid earth, by means of which the latter would retain some appreciable amount of gas. But if, as some believe, our atmosphere is about all that the earth can control,<sup>1</sup> the gas expelled from the molten sphere in excess of the mass of the present atmosphere would escape and be lost to the planet. Geological evidences—early Cambrian glaciation, Paleozoic periods of aridity, and the general testimony of life—all point toward the conclusion that early terrestrial atmospheric conditions were not radically different from those of today. If the hypothesis of a heavy atmosphere be not permissible, it becomes very difficult to explain the presence of original gases and gas-producing compounds in plutonic rocks on the basis of the Laplacian or other hypotheses that postulate original fluidity.

#### RELATIVE TO THE PLANETESIMAL HYPOTHESIS

After the gaseous matter of the ancestral sun was shot out from the solar surface to form the two arms of the spiral nebula, as postu-

<sup>1</sup> R. H. McKee, *Science*, Vol. XXIII (1906), pp. 271-74.

lated by the planetesimal hypothesis, the rock-producing portion is supposed either to have aggregated into planetesimal bodies, or to have been gathered, molecule by molecule, into the nucleus of the earth. The planetesimal bodies gathered in gas molecules of the atmospheric class both by chemical union and by surface adhesion or occlusion. As the earth grew by sweeping in the planetesimals, whatever gases they contained became entrapped in the body of the growing planet and well distributed throughout its mass. At first, the gravity of the earth may possibly have been able to hold only the gases brought in by planetesimal aggregates of rock material and those that became impounded in it by impact, but at a later stage, when increased mass enabled it to hold gaseous molecules, gases may have been added to the atmosphere directly from the nebula, and these, by chemical reactions, may have become united with the surface rocks. As soon as vulcanism commenced, a system of exchange was set up. While gases were being fed to the atmosphere by volcanic action, water, carbon dioxide, oxygen, and nitrogen were being buried with the surface rock material, partly by chemical union and partly by mechanical entrapment, as the growth by infalling matter continued. It is thus quite easy to understand how the earth came to be affected by these gases throughout its mass, and how they came to exist there in all available forms of retention.

While the carbon monoxide and methane derived from rocks by heating *in vacuo* are doubtless chiefly produced from the carbon dioxide and water present in the rock material, there seems good reason to suppose that similar reactions took place within the earth, as the surface material became buried and heated, and hence that carbon monoxide and methane exist, as such, in the earth's body, and are to be reckoned among the natural gases of the rocks.

#### RELATIVE TO ATMOSPHERIC SUPPLY

The fact that many of the igneous rocks are able to yield hydrogen from reactions between water and ferrous compounds, at high temperatures, indicates that the material of the earth's crust is in a condition of partial oxidation only. Near the center of the earth there is probably very little oxygen, and even up to the surface, barring the weathered mantle, the rocks are suboxidized. Yet the earth is surrounded by an oxygenated atmosphere. Since oxygen is not devel-

oped in the combustion-tube, and does not appear to exist as a free gas in igneous rocks, it is not likely that this constituent of the atmosphere has come directly as an exudation from the interior of the globe. It is to be sought, rather, in a dissociation or decomposition of compound gases by physical or organic agencies. Originally, enough oxygen was derived from water vapor, by physical means, to permit the beginning of plant life; after vegetation appeared, an abundant source of oxygen was found in the carbon dioxide.

The average gas content of igneous rocks, as determined by the analyses now made, may be used to test the competence of the rocks to yield the present atmosphere. Taking the average volume of nitrogen per volume of rock to be 0.05, which is probably nearer the truth than the figure 0.09 given in table 8<sup>1</sup> (owing to leakage of air), it would require the liberation of all the nitrogen in the outermost 70 miles of the earth's crust to produce the nitrogen in the present atmosphere. For an estimate of the amount of igneous rock necessary to yield the carbon dioxide which is now locked up in limestone and coal deposits, we may take Dana's figure of 50 atmospheres of this gas, and an average of 2.16 volumes of carbon dioxide per volume of rock. To produce these 50 atmospheres of carbon dioxide, it is found that a thickness of 66 miles of crust would have to be deprived of its carbon dioxide<sup>2</sup>—a figure which corresponds fairly well with the estimate for nitrogen. If the water of the rocks be placed at 2.3 per cent., a depth of 70 miles would supply the hydrosphere.

On the planetesimal hypothesis, gas has been supplied from the interior to the atmosphere ever since an early stage of the earth's growth, probably from the earliest stage at which an atmosphere could be held, which may be placed at the time when the earth's radius was about 2,000 miles. From this it appears that only a small fraction of the full gas-producing possibilities of the rocks of the earth was required to supply the atmosphere. The fact that gases are still being given forth through volcanoes, and that the ejected lavas still have gas-producing qualities, makes it clear that all the resources of the interior are not yet exhausted. The working qualities of the planetesimal hypothesis, therefore, do not seem to be found wanting in either past possibilities of supply, present output, or prospective reserve.

<sup>1</sup> *Ante*, p. 545..

<sup>2</sup> The limestones, of course, are not here included.